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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

Quarterly Progress Report, June 11—September 10, 1976

November 1976

Work Performed Under Contract EX-76-C-01-2018

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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

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11 June - 10 Sept. 1976

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ABSTRACT

A study of the reaction mechanism which leads to NO formation from fuel nitrogen by determining the rates and mechanisms of pyridine pyrolysis and cyanogen oxidation was continued. It was found that the rate of pyrolysis of C_5D_5N was about 90% of the pyrolysis rate of the normal pyridine. An isotope effect of this size is inconsistent with a non-chain reaction initiated by ring rupture. The oxidation of cyanogen appears to be first-order and zero-order with respect to cyanogen and oxygen respectively over a wide range of initial concentrations of these reactants. A possible mechanism to explain this rate law is being developed.

OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollution. The emission of NO and other oxides of nitrogen from various combustion devices is a serious contributor to that pollution. The source of NO during the combustion process may be atmospheric nitrogen or nitrogen-containing compounds in the fuel. In order to predict NO emission for the formulation of suitable analytical models, it is necessary to have accurate kinetic data and a reasonable reaction mechanism for the formation of NO.

The objective of this research program is to obtain kinetic and product distribution data from which a mechanism may be proposed for the formation of NO from fuel nitrogen. Specifically, the kinetics of the pyrolysis and oxidative pyrolysis of pyridine (since it is representative of the nitrogen-containing components of fossil fuels) will be studied. In addition, similar oxidative studies will be made on representative, condensed-ring heterocycles, e.g. quinoline, carbazole, etc. to determine the extrapolatability of the results obtained with pyridine to more coal like structures. The oxidation of volatile, nitrogen-containing pyridine pyrolysis products, e.g. cyanogen, HCN, vinylcyanide, etc., will also be carried out to help elucidate the mechanism of NO formation.

The experimental approach will involve the use of a stirred-flow reactor to obtain differential rate data which will aid in interpretation of complex kinetic data. On stream mass spectrometric, gas chromatographic and infrared spectrophotometric monitoring of products and reactants will be carried out also.

SUMMARY OF PROGRESS

Task 2, which consists of experiments to determine the rate and mechanism of pyrolysis of pyridine in an inert atmosphere, has been about 90% completed. No adjustment has been made to this figure during the report period because of equipment problems discussed in the details section. Some data measuring the isotope effect on the rate of pyrolysis was obtained. The effect was large enough so that a non-chain mechanism initiated by ring rupture could be excluded from consideration.

Task 4, which is concerned with the oxidation of nitrogen-containing intermediate species was continued with the study of the oxidation of cyanogen. The rate portion of the study is essentially complete. The reaction rate appears to be first-order in cyanogen and independent of oxygen concentration over a wide range of reactant concentrations. A material balance will now be investigated.

DETAILS OF TECHNICAL PROGRESS

Task 2

Work concentrated on better definition of the mechanism of pyridine pyrolysis (1). In an attempt to establish the initial step in the pyrolysis, the possibilities for which were discussed previously (1d), the isotope effect on the rate was measured by using C_5D_5N in place of the normal pyridine. The data are summarized in Table 1.

Table 1

Isotope Effect on Pyridine Pyrolysis Rate at 950°C

Contact Time (sec)	Initial Reactant Concentration (mole %)	% Reacted		
		C_5H_5N	C_5D_5N	Rate H/Rate D
0.5	1.0	19	14	1.36
1.0	0.5	38	14	2.71
1.0	2.0	53	48	1.10
2.0	0.5	60	40	1.50
2.0	2.0	69	50	1.38
				Av. 1.61

The rate difference for these two isotopic species is too large for the pyrolysis to be initiated by a simple ring rupture followed by a non-chain mechanism. However, it does not exclude a ring rupture-chain process where hydrogen atom abstraction is a propagation step. Additional isotope effect data will be obtained.

Following the acquisition of the data reported in Table 1, several equipment failures occurred sequentially. First, the temperature controller for the reactor ceased to function and had to be replaced.

Second, the on stream chromatograph thermister burned out and had to be replaced, accompanied by some circuit adjustments. Third, the departmental MS-GC had a major breakdown temporarily preventing the continuation of product investigations. The required repairs have delayed further studies on this reaction during this quarterly period and into the next. When operations are underway again, the major concerns will be the rate of production of HCN, better identification of the products, and the isotope effect over a temperature range.

Task 4

The rate of oxidation of cyanogen was measured at four additional sets of concentrations, in total eleven. The data from the first five sets were reported previously (1c), the last six are summarized in Table 2. Examination of these data shows that, although the scatter is large, a change in each reactant concentration of a factor of 16 reveals no trend in the apparent first-order rate constant (with respect to $(CN)_2$) at all three temperatures. The first-order constants are summarized in Table 3. Future effort will be directed toward examination of products and a material balance.

Table I

Oxidation of Cyanogen – Rate Data[a]

950°C

t_c/c_o	0.5/0.5			0.25/0.5			0.125/0.5		
	%	r x 10^3	r/c	%	r x 10^3	r/c	%	r x 10^3	r/c
0.25	5.2	10.08	.219	4.4	4.48	.181	6.6	3.20	.272
0.50	5.1	4.99	.108	5.7	2.89	.120	8.9	2.29	.196
1.0	6.3	3.03	.067	11.6	2.96	.131	10.9	1.39	.122
2.0	10.6	2.58	.059	16.8	2.14	.101	14.3	0.90	.082
3.0	17.3	2.81	.070	27.1	2.30	.124	30.0	1.28	.133

t_c/c_o	0.062/0.5			0.25/0.25			0.062/0.125		
	%	r x 10^3	r/c	%	r x 10^3	r/c	%	r x 10^3	r/c
0.25	4.6	1.18	.194	4.3	4.43	.181	3.4	0.82	.136
0.50	6.5	0.83	.139	3.7	1.91	.078	4.7	0.61	.098
1.0	13.4	0.85	.155	4.7	1.19	.069	10.2	0.69	.120
2.0	22.6	0.72	.146	13.8	1.04	.073	10.8	0.34	.061
3.0	45.5	0.96	.278	16.8	1.44	.067	18.0	0.38	.073

975°C

t_c/c_o	0.5/0.5			0.25/0.5			0.125/0.5		
	%	r x 10^3	r/c	%	r x 10^3	r/c	%	r x 10^3	r/c
0.25	5.8	11.12	.249	5.8	5.58	.245	3.5	1.70	.146
0.50	7.1	6.75	.153	8.6	4.15	.188	8.8	2.13	.194
1.0	10.8	5.16	.121	15.6	3.77	.184	15.6	1.89	.184
2.0	15.9	3.79	.095	25.2	3.05	.168	31.5	1.91	.226
3.0	27.1	4.30	.124	35.6	2.88	.184	35.7	1.45	.185

t_c/c_o	0.062/0.5			0.25/0.25			0.062/0.125		
	%	r x 10^3	r/c	%	r x 10^3	r/c	%	r x 10^3	r/c
0.25	4.8	1.16	.202	6.4	6.15	.271	5.5	1.34	.235
0.50	8.4	1.02	.184	9.3	4.50	.205	9.1	1.11	.201
1.0	20.1	1.22	.252	12.1	2.94	.138	18.8	1.13	.231
2.0	35.8	1.08	.278	18.1	2.19	.110	22.4	0.68	.144
3.0	46.5	0.94	.290	24.9	2.00	.111	28.3	0.57	.131

Oxidation of Cyanogen - Rate Data* (Continued)

1000°C

t_c \ c_{i_0}	0.5/0.5			0.25/0.5			0.125/0.5		
	f	$r \times 10^3$	r/c	f	$r \times 10^3$	r/c	f	$r \times 10^3$	r/c
0.25	10.5	19.42	.363	18.1	9.60	.459	8.0	3.73	.170
0.50	11.2	10.48	.231	13.0	3.01	.434	15.4	3.33	.154
1.0	16.1	7.81	.208	21.6	3.50	.368	23.9	2.80	.117
2.0	30.0	5.01	.213	35.2	4.12	.272	41.1	2.91	.178
3.0	39.4	6.11	.242	46.9	3.17	.231	50.3	2.21	.143

t_c \ c_{i_0}	0.062/0.5			0.25/0.25			0.062/0.125		
	f	$r \times 10^3$	r/c	f	$r \times 10^3$	r/c	f	$r \times 10^3$	r/c
0.25	9.8	.228	.436	5.2	1.91	.317	11.2	1.38	.370
0.50	16.7	.195	.400	11.1	3.28	.236	18.6	2.26	.461
1.0	24.9	.206	.336	16.3	3.83	.197	20.8	1.41	.262
2.0	44.3	.130	.303	28.8	1.36	.201	30.5	0.90	.218
3.0	62.0	.121	.334	37.3	2.89	.198	33.8	0.66	.170

*The symbols have the following significance:

t_c = contact time (sec).

c_{i_0} = reactor entrance concentrations (mole % in helium, $(CN)_2/O_2$).

f = percent cyanogen reacted.

r = rate of cyanogen consumption (mmole/liter-sec).

r/c = apparent first-order constant for cyanogen consumption (sec^{-1}).

Table 3

Apparent First-Order Rate
Constants for the Oxidation of Cyanogen

$C_0(CN)_2/C_0(O_2)$ (mole % in He)	k (sec^{-1}) 950°C	975°C	1000°C
0.5/2.0	0.101	0.160	0.264
0.25/2.0	0.193	0.260	0.482
1.0/1.0	0.093	0.145	0.228
0.5/1.0	0.108	0.184	0.263
0.25/1.0	0.117	0.120	0.228
0.5/0.5	0.105	0.148	0.270
0.25/0.5	0.132	0.194	0.379
0.125/0.5	0.163	0.187	0.366
0.062/0.5	0.182	0.241	0.464
0.25/0.25	0.090	0.167	0.206
0.062/0.125	0.098	0.188	0.367
	Av. 0.126	Av. 0.181	Av. 0.311

Tasks 1, 3, 5 and 6

Task 1 will be completed with the assembly of the quadrupole mass spectrometer, which has been postponed because of the other experiments currently being carried out; the other tasks will be undertaken at a later date.

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1. (a) T. Houser, "Fundamentals of Nitric Oxide Formation in Fossil Fuel Combustion," ERDA, FE-2018-1, QPR Period June - Sept. 1975.

   (b) ERDA, FE-2018-2, QPR Period Sept. - Dec. 1975.

   (c) ERDA, FE-2018-3, QPR Period Dec. 1975 - Mar. 1976.

   (d) ERDA, FE-2018-4, QPR Period Mar. - June 1976.

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